

08/17/99

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PTO/SB/05 (4/98)  
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# UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

Attorney Docket No. B-1482  
First Inventor or Application Identifier Yong Wang, et al.  
Title A method for steam reforming of a hydrocarbon  
Express Mail Label No. EJ017935648US

## APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO: Assistant Commissioner for Patents  
Box Patent Application  
Washington, DC 20231

1. ☒ \* Fee Transmittal Form (e.g., PTO/SB/17)  
(Submit an original and a duplicate for fee processing)
2. ☒ Specification [Total Pages 8]  
(preferred arrangement set forth below)
  - Descriptive title of the invention
  - Cross References to Related Applications
  - Statement Regarding Fed sponsored R & D
  - Reference to Microfiche Appendix
  - Background of the invention
  - Brief Summary of the invention
  - Brief Description of the Drawings (if filed)
  - Detailed Description
  - Claim(s)
  - Abstract of the Disclosure
3. ☒ Drawing(s) (35 U.S.C. 113) [Total Sheets 1]
4. Oath or Declaration [Total Pages 3]
  - a. ☒ Newly executed (original or copy)
  - b. ☐ Copy from a prior application (37 C.F.R. § 1.63(d))  
(for continuation/divisional with Box 16 completed)
    - i. ☐ DELETION OF INVENTOR(S)  
Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

5. ☐ Microfiche Computer Program (Appendix)
6. Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary)
  - a. ☐ Computer Readable Copy
  - b. ☐ Paper Copy (identical to computer copy)
  - c. ☐ Statement verifying identity of above copies

## ACCOMPANYING APPLICATION PARTS

7. ☒ Assignment Papers (cover sheet & document(s))
8. ☐ 37 C.F.R. § 3.73(b) Statement of Power of Attorney (when there is an assignee)
9. ☐ English Translation Document (if applicable)
10. ☐ Information Disclosure Statement (IDS)/PTO-1449 [Copies of IDS Citations]
11. ☐ Preliminary Amendment
12. ☒ Return Receipt Postcard (MPEP 503) (Should be specifically itemized)
13. ☒ \* Small Entity Statement(s) filed in prior application, Status still proper and desired (PTO/SB/09-12)
14. ☐ Certified Copy of Priority Document(s) (if foreign priority is claimed)
15. ☐ Other:

\* NOTE FOR ITEMS 1 & 13: IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37 C.F.R. § 1.27), EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).

16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No: \_\_\_\_\_  
Prior application information: Examiner \_\_\_\_\_ Group / Art Unit: \_\_\_\_\_

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

## 17. CORRESPONDENCE ADDRESS

☐ Customer Number or Bar Code Label (Insert Customer No. or Attach bar code label here) or ☒ Correspondence address below

Name Paul W. Zimmerman (K1-53)  
Battelle Memorial Institute  
Address P.O. Box 999  
City Richland State WA Zip Code 99352  
Country U.S.A. Telephone (509) 375-2981 Fax (509) 375-4487

Name (Print/Type) Paul W. Zimmerman Registration No. (Attorney/Agent) 34,761  
Signature Paul W. Zimmerman Date 09/AUG/17

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Y Wang, DP Vanderwiel, AY Tonkovich

For: A METHOD FOR STEAM REFORMING  
OF A HYDROCARBON

Our Ref. No: B-1482

Date: August 17, 1999

CERTIFICATE OF MAILING

Box PATENT APPLICATION  
Assistant Commissioner for Patents  
Washington, DC 20231

Dear Sir:

The undersigned hereby certifies that the attached:

- ☒ Patent Application of 8 pages
- ☒ 1 Sheets of Drawings
- ☒ Patent Transmittal Fee Sheet (2 ea.)
- ☒ Assignment and Cover Sheet
- ☒ Combined Declaration and Power of Attorney
- ☒ Small Entity
- ☐ Information Disclosure Statement
- ☐ with attachments

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*Janice K Laybourn*  
Signature

8/17/99  
Date Deposited

Janice K. Laybourn (K1-53)  
Intellectual Property Services  
Battelle Memorial Institute  
Pacific Northwest Division  
P.O. Box 999  
Richland, WA 99352  
(509) 375-2655

CHANNED 10

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant or Patentee: Yong Wang, David P. Vanderwiel, Anna Lee Y. Tonkovich

Serial or Patent No.: \_\_\_\_\_

Filed or Issued: \_\_\_\_\_

For: A METHOD FOR STEAM REFORMING OF A HYDROCARBON

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS  
(37 CFR 1.9(f) and 1.27(d)) - NONPROFIT ORGANIZATION

I hereby declare that I am an official empowered to act on behalf of the nonprofit organization identified below:

NAME OF ORGANIZATION Battelle Memorial Institute  
Pacific Northwest Division  
ADDRESS OF ORGANIZATION Post Office Box 999, Richland, WA 99352

TYPE OF ORGANIZATION:

[X] Nonprofit Scientific or Educational Under Statute of State of the  
United States of America  
(Name of State Ohio)  
(Citation of Statute Sections 1719.01 and 1719.05, Rev. Code  
of Ohio)

I hereby declare that the nonprofit organization identified above qualifies as a nonprofit organization as defined in 37 CFR 1.9(e) for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code with regard to the invention entitled A METHOD FOR STEAM REFORMING OF A HYDROCARBON by inventor(s) Yong Wang, David P. Vanderwiel, Anna Lee Y. Tonkovich described in

[ ] application executed \_\_\_\_\_  
[X] specification filed herewith  
[ ] application serial no. \_\_\_\_\_, filed \_\_\_\_\_  
[ ] patent no. \_\_\_\_\_, issued \_\_\_\_\_.

I hereby declare that rights under contract or law have been conveyed to and remain with the nonprofit organization with regard to the above identified invention.

If the rights held by the nonprofit organization are not exclusive, each individual, concern or organization having rights to the invention is listed below\* and no rights to the invention are held by any person, other than the inventor, who could not qualify as small business concern under 37 CFR 1.9(d) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

\*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

NAME NONE  
ADDRESS \_\_\_\_\_  
☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

NAME \_\_\_\_\_  
ADDRESS \_\_\_\_\_  
☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING Paul W. Zimmerman  
TITLE OF ORGANIZATION Contracting Officer, Pacific Northwest Division,  
Battelle Memorial Institute  
ADDRESS OF PERSON SIGNING Post Office Box 999, Richland, WA 99352

SIGNATURE Paul W. Zimmerman DATE 99/AUG/17

5           **A METHOD AND CATALYST STRUCTURE FOR STEAM REFORMING  
                  OF A HYDROCARBON**

                  FIELD OF THE INVENTION

10           The present invention is a method and catalyst structure for steam  
          reforming of a hydrocarbon.

                  BACKGROUND OF THE INVENTION

15           Steam reforming of hydrocarbons is commonly used for feedstock  
          production for carbon-monoxide hydrogenation (Fischer-Tropsch synthesis),  
          methanol synthesis and hydrogen production. Steam reforming is done  
          commercially by flowing a mixture of steam and the hydrocarbon past a  
          supported catalyst having an alumina support and a catalyst metal thereon, and  
20           reacting the mixture at a temperature from about 600 °C to about 1000 °C,  
          forming at least one product. Research has been done with the catalyst metal on  
          a spinel support. Residence times are typically on the order of seconds and  
          steam to carbon ratio greater than about 2.5. For steam to carbon ratio less than  
          2.5, catalyst activity is generally degraded after hours to days due to coke  
25           formation and the supported catalyst must be refreshed or replaced.

          The rate of supported catalyst activity degradation has been reduced by  
          use of excess steam (steam to carbon ratio greater than 2.5). Excess steam,  
          however, requires excess thermal energy and results in large system pressure  
          drop. Using less steam results in faster degradation of catalyst activity because  
30           of coking from the hydrocarbon(s).

Hence, there is a need for a method of steam reforming of a hydrocarbon that provides greater product yield and permits using less steam and maintaining catalytic activity of the catalyst.

5

## SUMMARY OF THE INVENTION

The present invention includes an improvement to the existing method of steam reforming of hydrocarbon, wherein the improvement comprises:

the flowing is at a rate providing a residence time less than about 0.1 sec resulting in obtaining product formation yield or amount that is the same or  
10 greater compared to product formation at a longer residence time.

Another improvement of the present invention is operation at a steam to carbon ratio that is substantially stoichiometric and maintaining activity of the supported catalyst.

The present invention also includes a catalyst structure for steam  
15 reforming of a hydrocarbon. The catalyst structure has

(a) a first porous structure with a first pore surface area and a first pore size of at least about 0.1  $\mu\text{m}$ ;  
(b) a porous interfacial layer that is a spinel with a second pore surface area and a second pore size less than the first pore size, the porous  
20 interfacial layer having a thickness less than 4 mm placed upon the first pore surface area;

(c) a steam reforming catalyst selected from the group consisting of rhodium, iridium, nickel, palladium, platinum, carbide of group VIb and combinations thereof placed upon the second pore surface area.

25 It is an object of the present invention to provide a method of steam reforming of hydrogen with a residence time of less than about 0.1 sec.

It is an object of the present invention to provide a catalyst structure with a porous interfacial layer of spinel.

The subject matter of the present invention is particularly pointed out and  
30 distinctly claimed in the concluding portion of this specification. However, both

the organization and method of operation, together with further advantages and objects thereof, may best be understood by reference to the following description taken in connection with accompanying drawings wherein like reference characters refer to like elements.

5

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph of conversion and selectivity versus temperature.

10

FIG. 2 is a graph of conversion and selectivity versus time.

## DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

15

The present invention includes a method for steam reforming of a hydrocarbon having the steps of flowing a mixture of steam and the hydrocarbon past a supported catalyst having a support and a catalyst metal thereon. The mixture is reacted at a temperature from about 600 °C to about 1000 °C forming at least one product. The improvement of the present invention is using a spinel support and flowing the mixture at a rate providing a residence time less than about 0.1 sec and obtaining product formation that is the same or greater than that obtained at longer residence times.

20

Also, under the previously described conditions, catalytic activity is degraded when the steam to carbon ratio is substantially stoichiometric. Another improvement of the present invention realized by flowing the mixture at a rate providing a residence time less than about 0.1 sec is maintaining activity of the spinel supported catalyst beyond 6 hours without degradation by coking even for substantially stoichiometric steam to carbon ratio. Substantially stoichiometric is a steam to carbon content ratio greater than about 0.9 and less than about 2.5, preferably from about 0.98 to about 2.

30

The supported catalyst may be in the form of a powder of non-porous particles, porous solid and combinations thereof.

Hydrocarbon includes oxygenates, alkanes, alkenes, alkynes, branched isomers, aromatics, saturated and unsaturated hydrocarbons and combinations thereof including fuels such as gasoline, kerosine, diesel, JP-8.

#### 5    Example 1

An experiment was conducted to demonstrate the present invention. The supported catalyst was spinel of a gamma-alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) support with a magnesia (MgO) passivation layer and rhodium oxide ( $\text{Rh}_2\text{O}_3$ ). The approximate composition was about 15 wt%  $\text{Rh}_2\text{O}_3$ , about 5 wt% MgO, and about 80 wt%  $\gamma\text{-Al}_2\text{O}_3$ . The supported catalyst was prepared by (1) calcining a high surface area  $\gamma\text{-Al}_2\text{O}_3$  at 500 °C for 5 hours; (2) impregnating the  $\gamma\text{-Al}_2\text{O}_3$  with MgO using the incipient wetness technique with a solution of magnesium nitrate; and obtaining an MgO modified  $\gamma\text{-Al}_2\text{O}_3$  support; (3) drying the modified support at 110 °C for 4 hours followed by (4) a second calcination at 900 °C for 2 hours; (5) impregnating the modified support with  $\text{Rh}_2\text{O}_3$  with the incipient wetness technique from a rhodium nitrate solution; (6) followed by a final drying 110 °C for 4 hours and a (7) a final calcination at 500 °C for 3 hours to obtain a powder of the supported catalyst.

A microreactor was constructed of a quartz tube with 4mm ID and 6.35 mm OD. About 0.2 g of powder of supported catalyst was placed in the microreactor in a packed bed arrangement.

Reactants were steam and methane in a steam to carbon ratio of approximately 1 which is stoichiometric within measurement uncertainty. Reactants were flowed through the reactor at temperatures from 650 °C to 900 °C.

Results are shown in **FIG. 1** for a steam to carbon ratio of 3 with conversion ranging from about 52% to 95% with increasing temperature and selectivity ranging from 22% to 70%.



Results in **FIG. 2** are for a steam to carbon ratio of 1 at 900 °C over 40 hours. No degradation of the supported catalyst was observed. Electron microscopic examination after testing revealed no coke deposition and BET measurements detected no significant loss in surface area.

5

## CLOSURE

While a preferred embodiment of the present invention has been shown  
10 and described, it will be apparent to those skilled in the art that many changes  
and modifications may be made without departing from the invention in its  
broader aspects. The appended claims are therefore intended to cover all such  
changes and modifications as fall within the true spirit and scope of the invention.

## CLAIMS

5

We claim:

1. A method for steam reforming of a hydrocarbon having the steps of flowing a mixture of steam and said hydrocarbon past a supported catalyst  
10 having a support and a catalyst metal thereon, and reacting said mixture at a temperature from about 600 °C to about 1000 °C forming at least one product; wherein the improvement comprises:

said support is a spinel support; and

said flowing is at a rate providing a residence time less than about 0.1 sec  
15 and obtaining said forming the same or greater compared to said forming at a longer residence time.

2. The method as recited in claim 1, wherein said mixture has a steam to carbon ratio less than 2.5, said improvement maintaining activity of said  
20 supported catalyst beyond 6 hours.

3. The method as recited in claim 1, wherein said spinel support controls acidity of said supported catalyst.

25 4. A method for steam reforming of a hydrocarbon having the steps of flowing a mixture of steam and said hydrocarbon having a steam to carbon ratio that is substantially stoichiometric past a supported catalyst having a support and a catalyst metal thereon, and reacting said mixture at a temperature from about 600 °C to about 1000 °C forming at least one product and degrading catalytic  
30 activity of said supported catalyst; wherein the improvement comprises:

said support is a spinel support; and

said flowing is at a rate providing a residence time less than about 0.1 sec and maintaining activity of said supported catalyst for said steam to carbon ratio less than 2.5.

5            5.     The method as recited in claim 4, wherein said support is spinel that controls acidity of said supported catalyst.

6.     The method as recited in claim 4, wherein said steam to carbon ratio is greater than about 0.9 and less than about 2.5.

10

7.     The method as recited in claim 4, wherein said supported catalyst is on a porous substrate.

8.     A catalyst structure for steam reforming of a hydrocarbon,  
15 comprising:

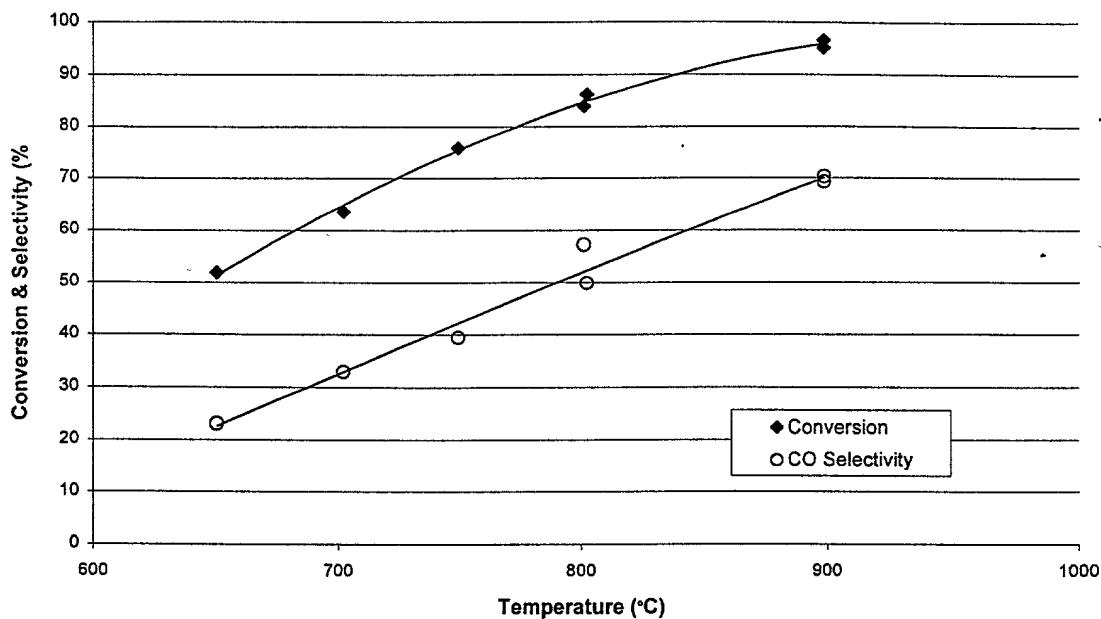
- (a)     a first porous structure with a first pore surface area and a first pore size of at least about 0.1  $\mu\text{m}$ ;
- (b)     a buffer layer upon said first pore surface area;
- (c)     a porous interfacial layer that is a spinel with a second pore surface area and a second pore size less than said first pore size, said porous interfacial layer having a thickness less than 4 mm placed upon said buffer layer;
- (d)     a steam reforming catalyst selected from the group consisting of rhodium, iridium, nickel, palladium, platinum, carbide of group IVb and combinations thereof placed upon said second pore surface area.

25

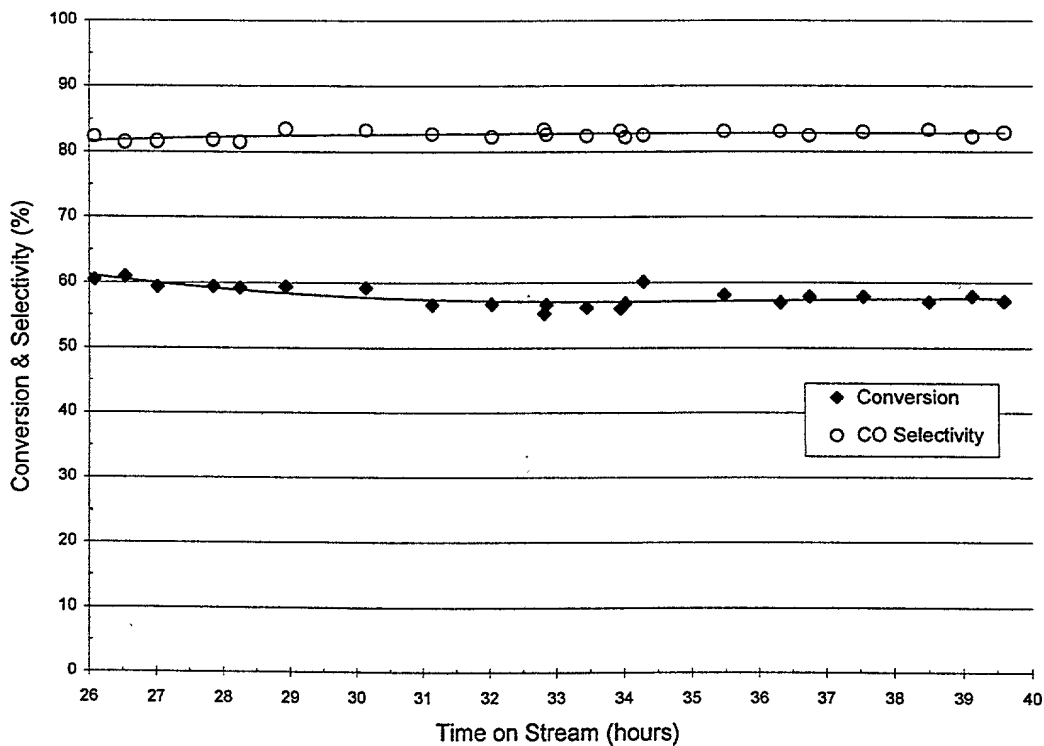
9.     The catalyst structure as recited in claim 8, wherein said carbide is selected from the group of tungsten carbide, molybdenum carbide and combinations thereof.

## ABSTRACT

The present invention includes an improvement to the existing method of  
5 steam reforming of hydrocarbon, wherein the improvement comprises: the  
flowing is at a rate providing a residence time less than about 0.1 sec  
resulting in obtaining product formation yield or amount that is the same or  
greater compared to product formation at a longer residence time. Another  
improvement of the present invention is operation at a steam to carbon ratio that  
10 is substantially stoichiometric and maintaining activity of the supported catalyst.  
The present invention also includes a catalyst structure for steam reforming of a  
hydrocarbon.



**Figure 1.** Steam reforming of methane over Rh/MgO/Al<sub>2</sub>O<sub>3</sub> (25-msec, H<sub>2</sub>O:CH<sub>4</sub> = 3:1)



**Figure 2.** Steam reforming of methane over Rh/MgO/Al<sub>2</sub>O<sub>3</sub> (25-msec, H<sub>2</sub>O:CH<sub>4</sub> = 1:1, 900°C)

COMBINED DECLARATION AND POWER OF ATTORNEY  
FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name,

I believe I am an original, first, and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled A METHOD FOR STEAM REFORMING OF A HYDROCARBON, the specification of which

☒ is attached hereto.

☐ was filed on \_\_\_\_\_ as  
Application Serial No. \_\_\_\_\_

☐ and was amended on \_\_\_\_\_  
(if applicable)

☐ with amendments through \_\_\_\_\_  
(if applicable)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, Sec. 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Sec. 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

☒ no such applications have been filed

☐ such applications have been filed as follows

Prior Foreign Application(s)

Priority  
Claimed

NONE

<u>                    </u>	<u>                    </u>	<u>                    </u>	<input type="checkbox"/> [ ]	<input type="checkbox"/> [ ]
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
<u>                    </u>	<u>                    </u>	<u>                    </u>	<input type="checkbox"/> [ ]	<input type="checkbox"/> [ ]
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
<u>                    </u>	<u>                    </u>	<u>                    </u>	<input type="checkbox"/> [ ]	<input type="checkbox"/> [ ]
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No

I hereby claim the benefit under Title 35, United States Code, Sec. 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Sec. 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, Sec. 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

NONE

<u>                    </u>	<u>                    </u>	<u>                    </u>
(Application Serial No.)	(Filing Date)	(Status - patented, pending, abandoned)
<u>                    </u>	<u>                    </u>	<u>                    </u>
(Application Serial No.)	(Filing Date)	(Status - patented, pending, abandoned)

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application, to file a corresponding international application, and to transact all business in the Patent and Trademark Office connected therewith:

Paul W. Zimmerman, Registration No. 34,761  
Stephen R. May, Registration No. 29,255

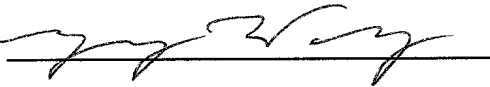
Address all correspondence to:

Stephen R. May K1-53  
Intellectual Property Services  
Battelle Memorial Institute  
Pacific Northwest Division  
Post Office Box 999  
Richland, WA 99352

Direct all phone calls to him at (509) 375-2387

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of first joint inventor Yong Wang

Inventor's signature  8/17/1999  
Date

Residence Richland, Washington

Citizenship China

Post Office address 2884 Troon Ct. Richland, WA 99352

Full name of second joint inventor David P. Vanderwiel

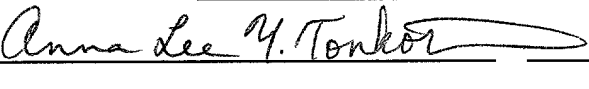
Inventor's signature  8-17-99  
Date

Residence Richland, Washington

Citizenship U.S.A.

Post Office address 2550 Duportail St.G-241, Richland, WA 99352

Full name of third joint inventor Anna Lee Y. Tonkovich

Inventor's signature  8-17-99  
Date

Residence Pasco, Washington

Citizenship U.S.A.

Post Office address 1604 North 37th Place North, Pasco, WA 99301